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Denitrogenative palladium-catalyzed coupling of aryl halides with arylhydrazines under mild conditions†

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The development of a method for the Pd(II)-catalyzed denitrogenative coupling of arylhydrazines to give functionalized biaryls in good yield, using aryl bromides or aryl iodides as convenient and inexpensive aryl sources, is reported. High functional group tolerance is demonstrated for electronically distinct arylhydrazines as well as aryl halides. The desired products were isolated in good to excellent yields for 58 examples. Control experiments and mechanism studies revealed that the transformation undergoes a base-promoted Pd-catalyzed process.

Introduction

Biaryls have attracted considerable attention due to their wide application in organic synthesis, advanced functional materials, and pharmaceuticals.[1] Enormous efforts have been devoted to developing efficient methods for building such a structure. Transition-metal-catalyzed cross-coupling reactions of aryl halides with arylmetallic reagents, such as Suzuki–Miyaura, Migita–Kosugi–Stille, Negishi, Kumada–Tamao–Corriu, and Hiyama reactions, constitute one of the most important and attractive research areas in both academia and industry, and provided powerful protocols to construct biaryls.[2]

The area of transition-metal-catalyzed cross-coupling reactions has experienced considerable growth in the past few decades. This strategy has created powerful and indispensable methods for selective construction of carbon–carbon/carbon–heteroatom bonds, as well as in synthesizing functional molecules and natural products.[3] To expedite synthetic endeavors, chemists have mainly focused on the development of new catalysts for various coupling reactions. On the other hand, the developments toward novel coupling partners also represent the major challenges in organometallic research area.

Recently, transition-metal-catalyzed cross-coupling *via* C–N bond cleavage has attracted considerable attention and versatile activated C–N bond containing partners, such as diazonium salts,[4] triazoles[5] and azaheterocycles[6] have been explored in cross-coupling reactions under transition metal catalysis. However, the existing methods still suffer from harsh reaction conditions, limited substrate scope and the poor stability of the substrates. Environmentally friendly aryl halide surrogates that function under mild reaction conditions with excellent chemo- and regioselectivities are still in great demand. On this basis, there is still a great requirement for developing new methods to cleave C–N bonds. Due to the stability and high dissociation energy of the C–N bond, arylhydrazines have recently become a hot topic as potential coupling partners.[7]

Arylhydrazine salts have been widely used for organic synthesis because of their stability, high reactivity, and availability.[8] On the other hand, despite the fact that arylhydrazines as readily available and extremely valuable reagents are widely used to prepare numerous nitrogen containing compounds and produce radical species *via* oxidation,[9] little attention has been paid to their use as arylating reagents *via* denitrogenation. Recently, pioneering work by Loh *et al.* demonstrated that an aryl hydrazine could be transferred into palladium species under aerobic oxidative reaction conditions, with N_2 and H_2O as the only byproducts.[10] As appealing environmentally benign surrogates for aryl halides, aryl hydrazines have been employed in a number of Pd-catalyzed coupling reactions (Heck-type,[11] Suzuki-type,[12] addition,[13] homocoupling,[14] *etc.*[15]) *via* C–N bond cleavage, although the use of these compounds in the coupling with aryl halides in organic transformations is still in its infancy.

The current coupling methods of arylhydrazines mainly relied on the application of acids as the promoter. The common catalytic course initially began with $L_2Pd(\text{II})A_2$ (A) which is formed by the oxidation of $Pd(0)L_2$ and an acid. Palladiaziridine complex B was easily generated in the presence of arylhydrazine and complex A. Oxidative insertion of

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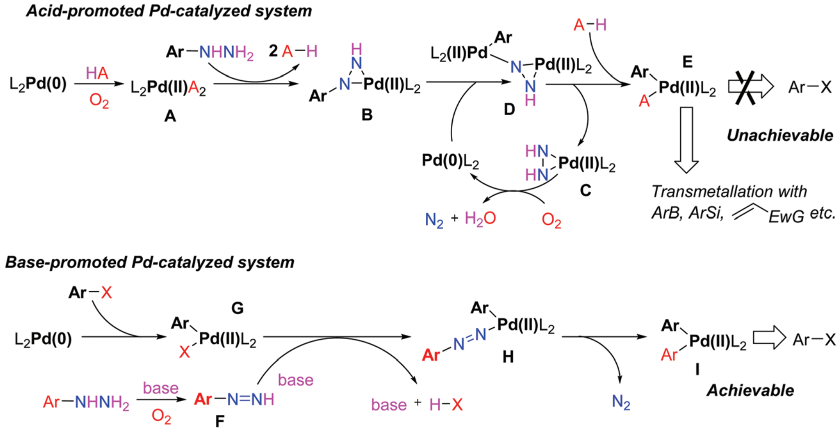
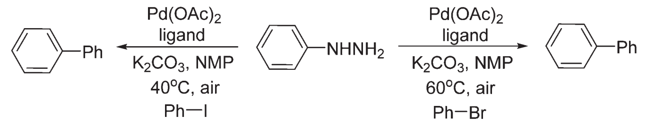


Scheme 1 The theoretical analysis of Pd-catalyzed coupling with arylhydrazine and aryl halide.

$Pd(0)L_2$ into complex **B** would generate the two palladium(II)-centered complex **D** *via* C–N bond cleavage. The following protonolysis of **D** resulted in the generation of the aryl palladium complex **E** and the palladiaziridine complex **C** that was subsequently decomposed into $Pd(0)L_2$, N_2, and H_2O by O_2. Intermediate **E** could undergo transmetallation with many coupling partners. However, the reaction of aryl palladium complex **E** with aryl halides was unachievable because further oxidative addition to the Pd(IV) complex was unrealistic. So we turned our attention towards the possibility of coupling with aryl halides *via* a base-promoted Pd-catalyzed mechanism. First, arylhydrazine is dehydrogenated in the presence of the base to produce diazene **F**. Meanwhile, the oxidative addition of $Pd(0)L_2$ to aryl halides took place to produce the aryl palladium(II) complex **G**. Transmetallation of diazene **F** to complex **G** with the assistance of a base results in the formation of intermediate **H**. Next, the aryl palladium complex **H** could be transformed to a diaryl palladium(II) intermediate **I** *via* the release of N_2 molecules. $Pd(0)L_2$ was then regenerated to complete the Pd(0)–Pd(II) cycle by reductive elimination. It might be an achievable process for the coupling of arylhydrazines with aryl halides (Scheme 1).

As part of our ongoing study on new coupling methods for the construction of C–C bonds,[16] herein we disclose the novel palladium-catalyzed C–C bond-forming reaction of various arylhydrazines with readily available aryl halides (aryl bromide and aryl iodide) using air as the green oxidant under basic reaction conditions *via* unactivated aryl C–N bond cleavage.

Table 1 Optimization of the Pd-catalyzed denitrogenative cross-coupling of phenyl halide with phenylhydrazine[a]



Entry	Ligand	Yield[b] (%)	Yield[c] (%)
1	—	13	21
2	$P(t\text{-Bu})_3$	45	52
3	PCy_3	55	50
4	$P(n\text{-Bu})_3$	33	39
5	$P(OPh)_3$	62	66
6	$P(OMe)_3$	38	34
7	$P[O(o\text{-tol})]_3$	69	75
8	PPh_3	68	80
9	$P(p\text{-tol})_3$	77	88
10	$P(m\text{-tol})_3$	88	86
11	$P(o\text{-tol})_3$	89	**95**
12	TFP	**92**	85
13	Dppp	67	64
14	Dppe	74	79
15	Dppm	61	73
16	Dppb	66	77
17	Dppf	68	67
18	Dmpe	52	45
19	BINAP	71	74

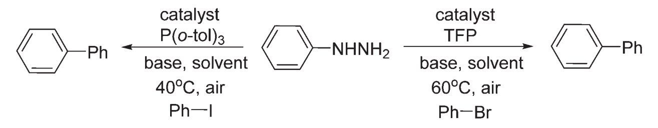
[a] Isolated yields. [b] Reaction conditions A: Phenylhydrazine (1 mmol), bromobenzene (1.1 mmol), $Pd(OAc)_2$ (2 mol%), ligand (3 mol%), K_2CO_3 (2.0 mmol), NMP (2 mL), 3 h. [c] Reaction conditions B: Phenylhydrazine (1 mmol), iodobenzene (1.1 mmol), $Pd(OAc)_2$ (2 mol%), ligand (3 mol%), K_2CO_3 (2.0 mmol), NMP (2 mL), 3 h.

Results and discussion

We commenced our studies by exploring reaction conditions for the envisioned Pd-catalyzed denitrogenative cross-coupling of bromobenzene with phenylhydrazine (Table 1, condition A). As expected, even after heating up to 120 °C, the desired coupling product could not be detected with an acid-promoted Pd-catalyzed system, using TFA as an acid in DMF under $Pd(OAc)_2$/dppp catalytic conditions. At the outset of our studies, bromobenzene and phenylhydrazine were reacted under the standard conditions commonly employed in the base-promoted Pd-catalyzed system using 2 mol% $Pd(OAc)_2$ as a catalyst and K_2CO_3 as a base in NMP (*N*-methyl pyrrolidine) at 60 °C (Table 1, entry 1). As expected, the desired coupling product could be obtained in a yield of 13%. We initially screened the combination of $Pd(OAc)_2$ and some common monodentate phosphine ligands. It should be noted that trialkyl phosphine ($P(t\text{-Bu})_3$, PCy_3, $P(n\text{-Bu})_3$) (Table 1, entries

2–4) and trioxy phosphine ($P(OPh)_3$, $P(OMe)_3$, $P[O(o\text{-tol})]_3$) (Table 1, entries 5–7) were less effective than triaryl phosphine for this reaction (Table 1, entries 8–12). Among the monodentate phosphine ligands tested, TFP (trifurylphosphine) was the most effective affording the cross-coupled product in 92% yield (Table 1, entry 12). We also tried bidentate phosphine ligands with $Pd(OAc)_2$ as the Pd source to determine the reaction efficiency. The ligands Dppp (1,3-bis(diphenylphosphino) propane), Dppe (1,2-bisdiphenylphosphinoethane), Dppm (1,1-bisdiphenylphosphinomethane), and Dppb (1,4-bisdiphenylphosphinobutane) instead of TFP were not suitable (Table 1, entries 13–16). The use of Dppf (1,1′-bisdiphenylphosphinoferrocene), Dmpe (1,2-bisdimethylphosphinoethane), or BINAP ((+/−)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) resulted in poor yields (Table 1, entries 17–19). To test the feasibility of this process in an iodobenzene system, we investigated the optimization of the reaction using iodobenzene as an aryl halide source with a phenylhydrazine substrate as a model substrate (Table 1, condition B). Subsequent attempts at lower temperature showed that an excellent yield can be achieved at 40 °C, and not much longer reaction time was required. Further optimization revealed that the reaction reached completion furnishing the desired product in 95% yield when $P(o\text{-tol})_3$ was employed.

Table 2 Further optimization of the Pd-catalyzed denitrogenative cross-coupling of phenyl halide with phenylhydrazine[a]



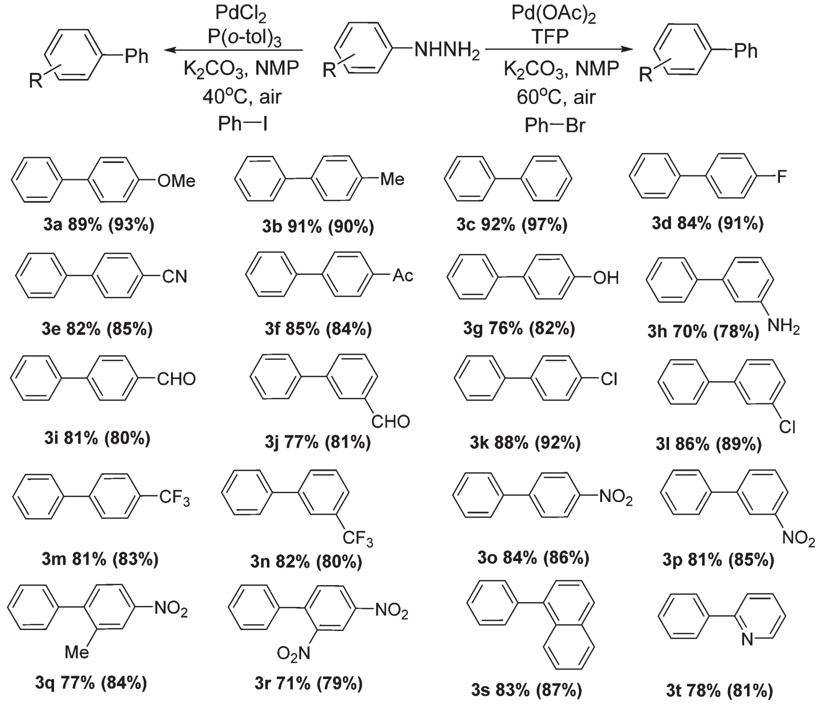
Entry	Solvent	Catalyst	Base	Yield[b] (%)	Yield[c] (%)
1	NMP	$Pd(OAc)_2$	K_2CO_3	**92**	95
2	DMSO	$Pd(OAc)_2$	K_2CO_3	71	77
3	DMF	$Pd(OAc)_2$	K_2CO_3	66	72
4	DMA	$Pd(OAc)_2$	K_2CO_3	69	67
5	Toluene	$Pd(OAc)_2$	K_2CO_3	55	69
6	Xylene	$Pd(OAc)_2$	K_2CO_3	59	58
7	CH_3CN	$Pd(OAc)_2$	K_2CO_3	47	58
8	THF	$Pd(OAc)_2$	K_2CO_3	51	52
9	DME	$Pd(OAc)_2$	K_2CO_3	42	63
10	NMP	—	K_2CO_3	—	—
11	NMP	$PdCl_2$	K_2CO_3	90	**97**
12	NMP	$Pd(TFA)_2$	K_2CO_3	86	90
13	NMP	$Pd(OTs)_2$	K_2CO_3	81	84
14	NMP	$Pd(dba)_2$	K_2CO_3	75	77
15	NMP	$Pd_2(dba)_3$	K_2CO_3	65	62
16	NMP	$Pd(PPh_3)_4$	K_2CO_3	58	65
17	NMP	$Pd(PPh_3)_3Cl_2$	K_2CO_3	83	88
18	NMP	$Pd(dppf)Cl_2$	K_2CO_3	86	85
19	NMP	$Pd(OAc)_2$	Cs_2CO_3	71	70[d]
20	NMP	$Pd(OAc)_2$	Na_2CO_3	74	78[d]
21	NMP	$Pd(OAc)_2$	KOAc	68	76[d]
22	NMP	$Pd(OAc)_2$	NaOAc	61	75[d]
23	NMP	$Pd(OAc)_2$	NaOH	35	44[d]
24	NMP	$Pd(OAc)_2$	KOH	38	42[d]

[a] Isolated yields. [b] Reaction conditions A: Phenylhydrazine (1 mmol), bromobenzene (1.1 mmol), catalyst (2 mol%), TFP (3 mol%), base (2.0 mmol), solvent (2 mL), 60 °C, 3 h. [c] Reaction conditions B: Phenylhydrazine (1 mmol), iodobenzene (1.1 mmol), catalyst (2 mol%), $P(o\text{-tol})_3$ (3 mol%), base (2.0 mmol), solvent (2 mL), 40 °C, 3 h. [d] Using $PdCl_2$ as the catalyst.

Optimization with respect to solvents, catalysts, and bases was explored under these reaction conditions (Table 2, condition A). Subsequent studies of bromobenzene in the presence of potassium carbonate (2 equiv.), TFP (3 mol%) and palladium acetate (2 mol%) showed that *N*-methyl pyrrolidine (NMP) effectively facilitated the reaction and 92% of the desired product was obtained (Table 2, entry 1). This improvement is in agreement with the positive effect of NMP observed in a number of organic reactions. Interestingly, none of the other high boiling point solvents examined afforded the product in significant yield (Table 2, entries 2–6). The screening of other solvents, such as CH_3CN, THF, and DME (dimethoxyethane), gave modest yields (Table 2, entries 7–9). The reaction failed to proceed in the absence of the palladium catalyst (Table 2, entry 10), suggesting that the palladium catalyst is very crucial for the formation of biaryl compounds. As detailed in Table 2, the optimal conditions for the denitrogenative coupling can be applied toward the use of other palladium catalysts. It was observed that most of the palladium catalysts could successfully promote the reaction. Therefore, $PdCl_2$, $Pd(TFA)_2$ and $Pd(OTf)_2$ in combination with TFP were applied affording biphenyl in yields varying between 81% and 90% (Table 2, entries 11–13). It should be noted that $Pd(dba)_2$, $Pd_2(dba)_3$ and $Pd(PPh_3)_4$ were less effective than $Pd(OAc)_2$ for this reaction (Table 2, entries 14–16). The introduction of various palladium catalysts with phosphine ligands ($Pd(PPh_3)_3Cl_2$ and $Pd(dppf)Cl_2$) didn't increase the yields (Table 2, entries 17 and 18). Finally, the influence of a base was studied (Table 2, entries 19–24). Potassium carbonate proved superior, though cesium carbonate and sodium carbonate afforded low yields of the coupled product (Table 2, entries 19 and 20). Reactions with sodium acetate, potassium acetate, sodium hydroxide, and potassium hydroxide afforded only modest amounts of products (Table 2, entries 21–24). Then further optimization with respect to solvents, catalysts, and bases was explored with iodobenzene (Table 2, condition B). Thus, the optimized conditions can be summarized as $Pd(OAc)_2$/TFP as the catalyst, additive K_2CO_3, using bromobenzene as the substrate, and $PdCl_2/P(o\text{-tol})_3$ as the catalyst, and K_2CO_3 as the base using iodobenzene as the substrate (Table 2, entry 26).

Having gained preliminary insight into this novel reaction and identified the optimized reaction conditions, we next explored the scope and generality of this process. With the best optimized reaction conditions in hand ($Pd(OAc)_2$/TPE/K_2CO_3 and $PdCl_2/P(o\text{-tol})_3/K_2CO_3$), we began to the evaluation of the substrate scope of the denitrogenative Pd-catalyzed coupling of bromobenzenes and various arylhydrazines (Table 3, condition A). Using arylhydrazines with either electron-donating (Table 3, **3a–3b**) or electron-withdrawing groups (Table 3, **3d–3f**) at the *para*-position led to the formation of the corresponding biaryl derivatives in good to excellent yields in all the cases. Interestingly, phenylhydrazine substituted with a hydroxy or amino substituent furnished exclusively the desired product without the detection of the by-product

Table 3 Scope of the Pd-catalyzed denitrogenative cross-coupling of phenyl halides with various arylhydrazines



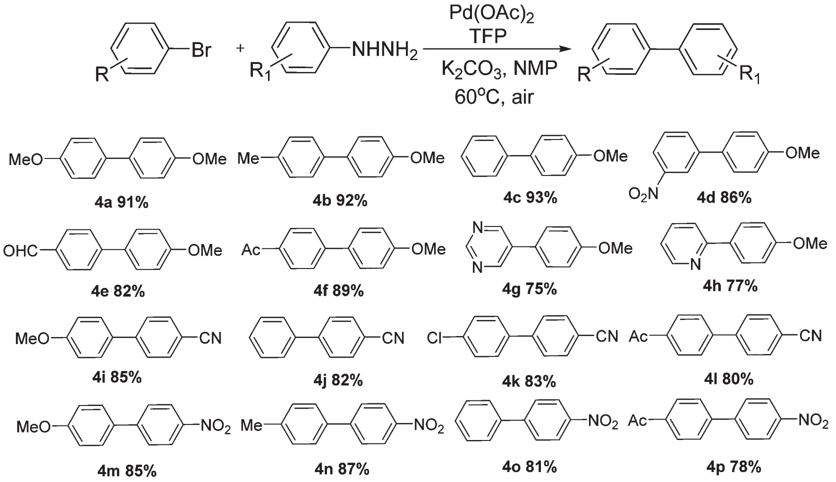
Reaction conditions A: Arylhydrazine (1 mmol), bromobenzene (1.1 mmol), $Pd(OAc)_2$ (2 mol%), TFP (3 mol%), K_2CO_3 (2.0 mmol), NMP (2 mL), 3 h. Reaction conditions B (in brackets): Arylhydrazines (1 mmol), iodobenzene (1.1 mmol), $PdCl_2$ (2 mol%), P(*o*-tol)$_3$ (3 mol%), K_2CO_3 (2.0 mmol), NMP (2 mL), 3 h.

(Table 3, **3g–3h**). Remarkably, a number of synthetically useful functionalities, including aryl fluoride, nitrile and aldehyde groups, were tolerated under the reaction conditions (Table 3, **3d–3g**). Notably, when the chloro phenylhydrazine is used, the corresponding denitrogenative coupling product is obtained in high yield, suggesting that the chloride leaving group in the arylhydrazine could survive (Table 3, **3k–3l**). In the case of a phenylhydrazine substituted with an aldehyde, chloro and trifluoromethyl group at the *meta*-/*para*-position, the yields of substrates with varied positions had no obvious differences (Table 3, **3i–3n**). When a series of nitro-substituted arylhydrazines were introduced, the corresponding products were obtained in moderate to good yields (Table 3, **3o–3r**). Next, this reaction was extended with naphthalen-1-ylhydrazine and found to produce the corresponding coupling derivative in good yield (Table 3, **3s**). Gratifyingly, this reaction could also be applied to the synthesis of 2-phenyl pyridine, albeit in a moderate yield (Table 3, **3t**). After having observed the general reactivity of arylhydrazines with bromobenzenes, we turned our attention to the reactivity of arylhydrazines with iodobenzene in lieu of bromobenzene for comparison (Table 3). The corresponding yields are shown in brackets.

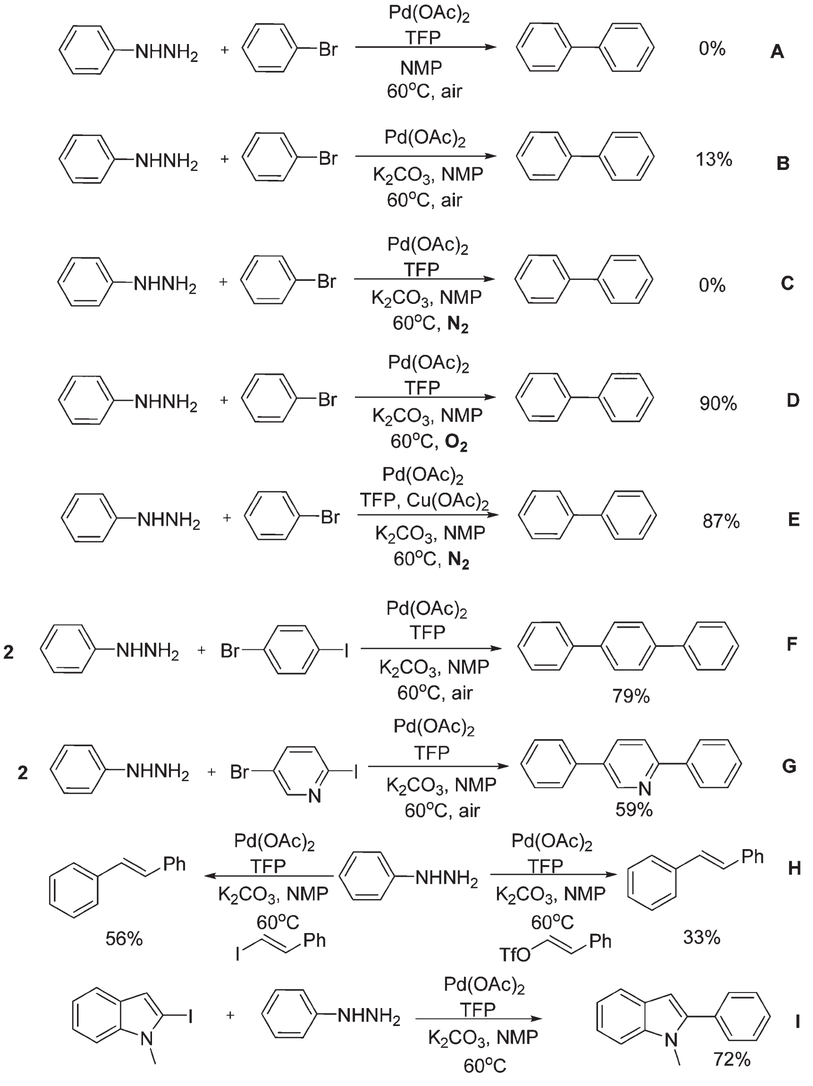
After achieving the coupling of different arylhydrazines with bromobenzene/iodobenzene, we further investigated the direct reaction of various aryl bromides under similar reaction conditions (Table 4). The reaction of electron-rich 4-methoxy phenylhydrazines proceeded smoothly with a series of *para*-/*meta*-substituted aryl bromides under the same reaction conditions as mentioned above, thus affording the corresponding coupling products in good yields (Table 4, **4a–4f**). Diverse aryl bromides with electron-withdrawing and electron-donating groups can undergo the reaction smoothly, with the corresponding products isolated in good to excellent yields (Table 4, **4a–4d**). The carbonyl groups acetyl, and formyl survived (Table 4, **4e–4f**); the functional groups –Me, –OMe, and $-NO_2$ at the *p*-/*m*-position in arenes imparted moderate reactivity furnishing **4a–4d** in acceptable yields. Some heterocycles are also compatible with our conditions, with 5-(4-methoxyphenyl)pyrimidine and 2-(4-methoxyphenyl)pyridine being produced in modest yields (Table 4, **4g–4h**). *p*-Cyan phenylhydrazines were thus chosen for the reaction instead of 4-methoxy phenylhydrazines (Table 4, **4i–4l**). Thus the scope was broad, and we found that 4-nitro phenylhydrazine substrates with *para*-functionalization furnished products in high yields, and with moderate to good yields (Table 4, **4m–4p**).

The possible mechanism of the palladium catalytic system was further verified by a series of control experiments (Scheme 2). Both base and ligand were indispensable to this transformation, which indicated that the reaction proceeded under base-promoted ligand-assisted Pd(II) catalysis (Scheme 2A and B). Otherwise, no desired products were detected under nitrogen and no better result was obtained

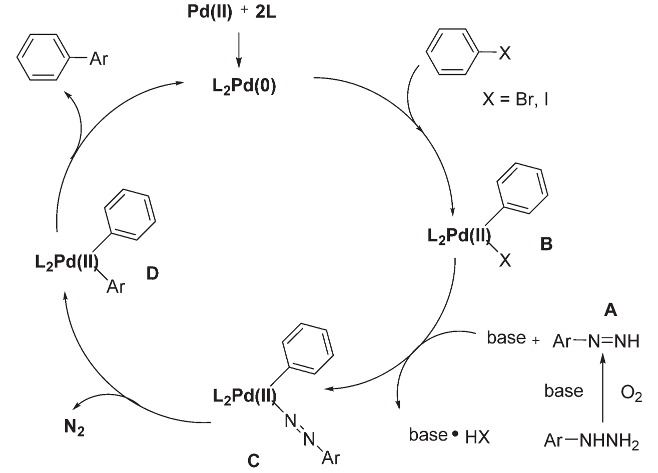
Table 4 Scope of the Pd-catalyzed denitrogenative cross-coupling of various aryl bromides with arylhydrazines



Reaction conditions: Arylhydrazines (1 mmol), aryl bromides (1.1 mmol), $Pd(OAc)_2$ (2 mol%), TFP (3 mol%), K_2CO_3 (2.0 mmol), NMP (2 mL), 3 h.



Scheme 2 Control experiments of the coupling reaction.



Scheme 3 Possible mechanism.

under pure oxygen (Scheme 2C and D). In the absence of oxygen, the application of 1 equiv. of $Cu(OAc)_2$ as an oxidant had no influence on the reaction and afforded the product in similar yields under ambient atmosphere (Scheme 2E). Notably, both bromo- and iodo-substituents on the same substrates were all reactive under the standard conditions. The direct coupling reaction between 2 equiv. of phenylhydrazine and 1-bromo-4-iodobenzene could afford terphenyl in 79% yield (Scheme 2F). The yield of 2,5-diphenylpyridine from 5-bromo-2-iodopyridine with 2 equiv. of phenylhydrazine was reduced to 59%, without the detection of the mono coupling product (Scheme 2G). Further application of this method was also investigated, (*E*)-(2-iodovinyl)benzene and (*E*)-styryl trifluoromethanesulfonate were used under our reaction conditions. The corresponding (*E*)-1,2-diphenylethene was isolated with yields of 56% and 33% (Scheme 2H). The reaction with valuable 2-iodo-*N*-methylindole was also tested, and 72% yield of 2-phenyl-*N*-methylindole was obtained (Scheme 2I).

A plausible reaction mechanism is outlined in Scheme 3; this mechanism is based on the procedure of the reported base-promoted coupling and the results of our experiments. First, arylhydrazine is dehydrogenated in the presence of the base in air to produce diazene product **A**. Oxidative addition of aryl halide to the *in situ* generated Pd(0) catalyst results in the formation of intermediate **B**. The transmetallation of intermediate **B** with diazene **A** by the assistance of a base cleaves the C–N bond to give palladium(II)-centered complex **C**. Complex **C** collapses to give diarylpalladium species **D** and nitrogen gas in the presence of oxygen. Reductive elimination of **D** results in the formation of the biaryl product and regenerates the palladium catalyst.

Conclusions

In summary, a novel, simple, and efficient protocol for the synthesis of biaryls *via* a Pd(II)-catalyzed denitrogenative coupling of arylhydrazines and aryl halides under ambient atmosphere and mild conditions has been developed. This process provides concise and highly practical access to biaryls, aryl bromides and aryl iodides and serves as cost-effective and convenient aryl sources for a broad range of substrates in up to 97% yield. Mechanism studies and control experiments revealed that the transformation undergoes a base-promoted Pd-catalyzed process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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